1
Introduction

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1.1 RATIONALE

Developments in the area of analytical chemistry have a very key role in almost all aspects of commerce, environmental science, and health science. Analytical measurements serve to confirm hypotheses as well as generate new ones. The evolution of analytical methodologies reflects a counterbalance between advances in the capabilities of basic instrumentation and its components and the demands for qualitative and quantitative information for a particular sample (analyte) system. The first of these aspects is driven by technology. The development of new optical sensors in atomic and molecular spectroscopy and high field magnets for FT-NMR or MS are examples of such advances. The other component in this process is the constant introduction of new analytical samples and the need for new types of information. For example, the development of higher density electronic devices and flat panel displays requires the ability to perform spatially resolved analyses with greater sensitivities than required of previous devices. Further, there is a need for analytical methodology for monitoring civil risks in the environment and for healthcare-related tasks, and for enabling progress in the biosciences. Eventually, analytical challenges outpace the capabilities of existing instrumentation, hence new methodologies must be developed. New challenges do not necessarily require the invention of new 'wheels'; simple retooling may produce improved capabilities. The analytical applications of glow discharge (GD) devices described herein are based on using well characterized technologies which have evolved over the last 100 years or so [1,2] to permit new capabilities for solving new problems. Specifically, low pressure, glow discharge plasmas are now

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employed to address challenges in the materials, biological, and environmental chemistry arenas.

Since the early 1970s, the use of glow discharge sources has been principally focused in the area of alloy characterization. Based primarily on the design concepts first described by Grimm [3], the sources were employed as higher precision alternatives to atmospheric pressure arc and spark emission sources. The forte of the devices is their ability to allow the direct elemental analysis of materials in the solid state. The 1980s brought about a number of studies that illustrated the more substantial capabilities to perform depth-resolved elemental analysis of 'thick' metal layers such as galvanized coatings [4,5]. The scope of application in solids was brought full-spectrum with the advent of radio frequency (rf) powering schemes in the 1990s that allow the direct analysis of nonconductive coatings and bulk insulators [6]. These basic capabilities for solids analysis are now realized in steady growth in sales of commercial instrumentation.

Recent studies described in the scientific literature have suggested very new applications of glow discharge spectroscopies not imagined a decade ago, including polymer mass spectrometry, sensitive determinations of nonmetals, and very thin ($<0.1\ \mu$m) film analysis. Figure 1.1 is a graph of the number of publications appearing in the literature describing the use, development, and study of glow discharge devices used in analytical spectroscopy over the decade 1991–2000. These data were compiled by the authors through queries on the Web of Science (Institute for Scientific Information) and, although some papers were surely overlooked, they should be a fair reflection of activity in the area. The data are broken down for each year according to whether the essence of the studies

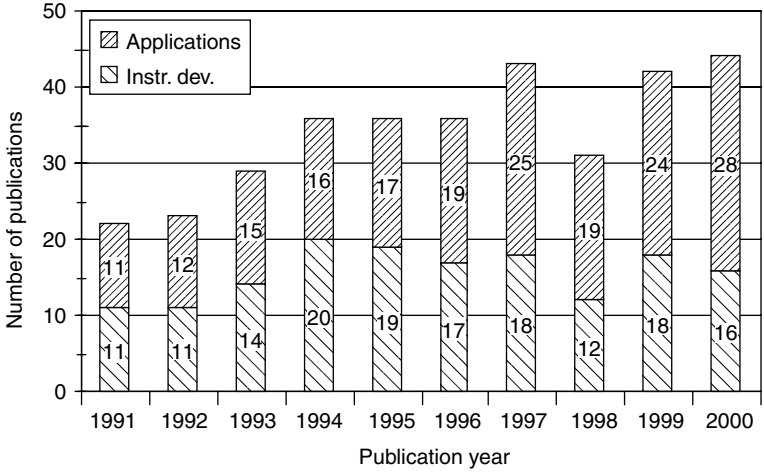

Figure 1.1 Number of publications describing instrumentation developments and applications of glow discharge sources from 1991 to 2000

was directed at the development of GD-based instrumentation or in the area of analytical applications of existing instrumentation. As can be seen, the total number of publications has nearly doubled over the last 10 years, with the lion's share of the growth in papers being carried by the applications category. This is a sign that the early-year research, taking place most often in academic laboratories, is being adopted in industrial laboratories. This is also reflective of the increase in sales of commercial instruments. While the absolute number of publications pales in comparison with those of most other atomic spectroscopic methods, the growing acceptance of GD methods is definitely being felt in many industries, as outlined throughout this book.

Certainly direct solids elemental analysis has been the 'bread and butter' of glow discharges for many decades, but there is a salient wave of application of glow discharge sources that should be noted here. The need for more extensive pieces of chemical information has led to new ways of looking at the glow discharge as an excitation and ionization source. As detailed in Chapters 13–17, the low pressure plasma has an advantageous combination of low kinetic (thermal) temperature with a high excitation temperature that affords the ability to provide both atomic and molecular species information not provided by atmospheric pressure plasmas and flames. In addition, the devices are easily coupled to many forms of gaseous sample introduction, such as gas chromatography. Creative methods of solution sample introduction have also been realized. Given the need for new methodologies for performing the so-called 'speciation' experiment, developments in this area are growing fast and are highlighted herein as a sign of their projected future impact.

Overall, it is the purpose of this book to outline the developments in analytical applications of glow discharge devices over the last decade and to highlight future trends as the techniques continue to evolve. Experts in the various applications of glow discharge devices have contributed to this volume and put their own applications into perspective with competing and complementary methods. It is hoped that the reader will begin to gain an appreciation for the fundamental processes occurring in glow discharges and also the scope of the current, and expected, analytical applications.

1.2 GLOW DISCHARGE DEVICES: BASIC OPERATING PRINCIPLES

Glow discharge devices are traditionally defined as reduced pressure, inert atmosphere, gaseous conductors [7]. The glow discharge is just one of many forms of gaseous discharges, often called plasmas. Figure 1.2 depicts the characteristic current–voltage relationships that exist for a number of diode-type discharges [8]. Each of these devices operates on the premise of having two distinct electrodes in a gaseous medium, between which electrical current is passed, the cathode having a negative potential and anode having a positive potential. In reality, these

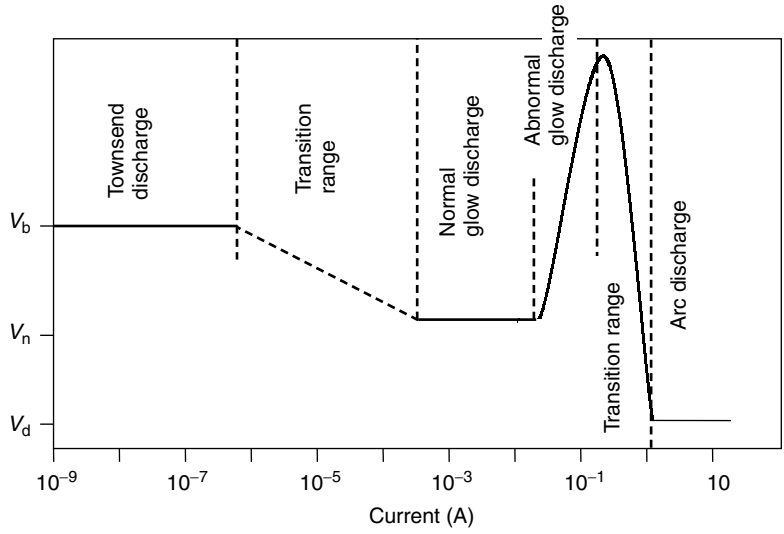

Figure 1.2 Current–voltage ($i-V$) characteristics of direct current (dc) electrical discharges

discharges are formed by potential differences, and so the designation of the two electrodes is simply based on relative potentials. In the figure, the increase in current (moving from left to right) can also be equated to operation pressure. Of the three major classifications, the Townsend discharge, the glow discharge, and the arc discharge, only the last two have been applied extensively in analytical chemistry. In Figure 1.2, V_b is the breakdown voltage, V_n is the normal operating voltage, and V_d is the operating voltage of arc discharge.

The electrical characteristics of a gas discharge can be best understood by beginning with the Townsend discharge regime. This discharge is generally operated in the sub-millitorr pressure regime and is characterized by having only a small degree of ion and free electron production. Following the Townsend discharge is a transition region, resulting from the increased energy exchange through collisions (due to higher gas pressures), wherein the electrical current increases while actually decreasing the required discharge maintenance voltage. This is a basic characteristic of a self-sustained discharge.

After the transition region, a luminous glow forms between the electrodes and is thus named a 'glow discharge'. At the onset of the glow discharge regime, increases in the current do not change the current density because the cathode surface is only partially covered by the discharge; as such, no increase in voltage is required. This is classified as the 'normal' glow discharge regime. As the current is further increased, the discharge glow will eventually cover the entire cathode surface. At this point, any increases in discharge current will result in an increase in current density, requiring an increase in the discharge

voltage. Plasmas that display this type of increasing $i-V$ relationship are termed 'abnormal' glow discharges. It is the abnormal glow discharge mode that is used most often in atomic spectroscopy. Analytical glow discharge devices generally operate in reduced pressure (0.1–10 Torr), inert gas atmospheres and at powers of less than 100 W. At the publication of this volume, it has now become clear, in fact, that plasmas operating in the glow discharge realm of voltage and current response can exist at atmospheric pressure [9].

As the discharge current is increased further in the glow discharge, the current density becomes so high that intense heating of the cathode through bombardment by filler gas ion species causes thermal vaporization of the cathode. Under these conditions, the production of high number densities of analyte atoms perturbs the potential fields and the $i-V$ characteristics of discharge become 'normal', i.e. the current then increases while decreasing the required discharge voltage, as is the situation for a dc arc. Usually operating at atmospheric pressure, the dc arc is characterized by its large currents and bright discharge plasma. At typical operating currents, 10–1000 A, the cathode surface is heated to the point that thermionic electron emission becomes a prominent current carrying mechanism. The combination of high vaporization rates and collisionally energetic plasma has made dc arcs a mainstay in analytical spectrochemical analysis of metallurgical samples [10,11].

A depiction of the simplest source geometry and plasma structure is presented in Figure 1.3 [7]. A glow discharge is initiated by the application of a sufficiently

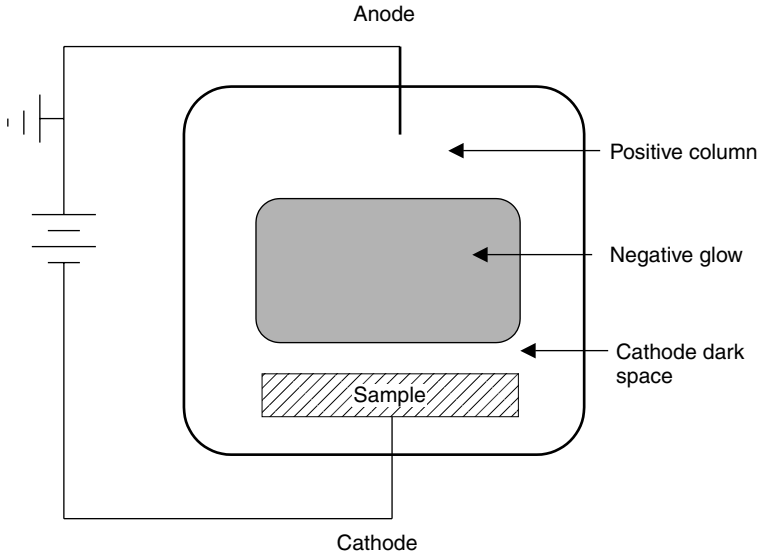

Figure 1.3 Simple diode geometry employed for glow discharge devices employed in spectrochemical analysis

high voltage between two electrodes in contact with the discharge gas (typically Ar). The potential difference (250–2000 V) causes the breakdown of the discharge gas to form positively charged ions and free electrons. The relative potentials on the cathode (−) and anode (+) result in the establishment of electric field gradients such that positively charged ions are accelerated to the cathode surface. The impinging ions transfer their momentum to the surface and lattice atoms, setting off a cathodic sputtering event. The products of the sputtering process are ejected atoms and small clusters of cathode material, ionic species, and secondary electrons. The process of cathodic sputtering is the means of solid sample atomization and the basis for depth-resolved analyses. In comparison with high vacuum sputtering of the sort employed in secondary ion mass spectrometry (SIMS), the GD source has much greater current densities (100s mA/cm^2 vs 1 μA/cm^2) and far lower average kinetic energies ($<$100 eV vs $>$1 keV) than typical 'ion guns'. As a result, sample ablation rates are much higher, but with far less lattice damage for the GD sputtering. The analytical consequences of these characteristics are highlighted throughout the following chapters.

Secondary electrons emitted in the sputtering process are essential in sustaining the discharge through gas phase ionization of sputtered material and discharge gas atoms. The negative potential of the cathode surface accelerates the electrons across the cathode dark space and into the negative glow region. Beyond direct ionization events, thermalized electrons are efficient at producing excited state atoms of the sputtered and discharge gas atoms. Evidence of these electron impact collisions is seen in the characteristic luminosity of the negative glow. Depending on the means of powering the GD, electrons in the negative glow can have temperatures of $>$5 eV; as such, they are very effective in populating high-lying excited states of nonmetal analytes such as H, C, and S. These sorts of electron energies are much higher than those found in atmospheric pressure plasmas and flames, while at the same time existing in an environment whose kinetic temperature is typically less than 500 K. Important also in the bulk plasma ionization are Penning-type collisions between highly excited, metastable discharge gas atoms and neutral atoms of the sputtered material. The result of these collisions is the formation of ions of the sputtered atoms that can be detected mass spectrometrically. The greatly increasing application of glow discharge devices (and reduced-pressure plasmas in general) as detectors for gaseous and solution-phase samples capitalizes on these gas-phase processes and conditions rather than in the ability to convert solid specimens into gas-phase populations which is essential to solids analysis.

1.3 GLOW DISCHARGE DEVICES: SCOPE OF APPLICATION

As suggested in the previous sections, the application of glow discharge devices as spectrochemical sources is increasing in diversity. It is important to realize, as with all other things in life, that 'one size does not fit all'. There are

a number of different discharge (electrode) geometries and powering schemes. There are also a variety of means of introducing the analytical sample depending on its state of matter: solid, liquid, or gas. In addition, analyte species within the discharge volume can be detected by many different spectroscopic methods including atomic absorption and fluorescence, optical emission, mass spectrometry, and a number of laser-based optical methods. In the case of optical emission spectrometry, the responses of component elements allows for the determination of the empirical formulae of 'molecular' analytes. Furthermore, molecular analytes can be determined directly by mass spectrometry where the spectra obtained can contain signatures representative of the molecular ion and structurally significant fragments. While this presentation may give the impression that each analysis employing a GD is unique in its own right, this is not the case. Instead, the experimental apparatus and methods can be quite routine, and this variability is simply a reflection of the inherent versatility afforded by the devices.

As described in the chapters that follow, at this stage in the evolution of analytical glow discharge sources there is a firm user base in the area of bulk and depth-resolved elemental analysis of metals and alloys by glow discharge optical emission spectroscopy (GD-OES). There are fewer actual instruments in the field of glow discharge mass spectrometry (GDMS), but the technique holds a unique place in the landscape of elemental analysis as providing sensitivity not afforded by any other conventional method of solids analysis. The scope of application of both of these methods is now being greatly expanded with the advent of rf powering schemes, wherein the direct analysis of insulating layers and bulk nonconductors is now possible. All of these sorts of applications rely on the two-step process of sputter atomization followed by gas-phase excitation/ionization. Some of the most exciting new applications employ the GD simply as an excitation/ionization source for samples introduced into the vapor phase. Strategies now exist, and are quickly evolving, wherein analytes originating in either the gaseous or solution phase can be introduced into reduced pressure plasmas, including inductively coupled plasmas. In this way, the discharges afford a great range of chemical information that is vital for applications in biological and environmental chemistry. In many respects, this well-aged source is finding many new lives to lead.

1.4 VOLUME OUTLINE

In an effort to cover the most relevant applications of glow discharge spectroscopies in the most informative way, the chapters of this volume have been written by acknowledged research and application leaders in the respective areas. It is these people who are the most up to date with literature coverage and can provide the most insight into how GD sources are designed and implemented for that particular field. The chapters have been arranged so as to build first on the

fundamentals of glow discharge operation, discuss the general application of the devices in the various atomic spectrometric modes, and then to look at specific fields of application. Most of the later chapters treat for the first time the rapidly evolving use of glow discharge and other forms of reduced pressure plasmas for solution and gaseous sample analyses. In this regard, it is hoped that the reader will gain new appreciation and insight into the next generation of glow discharge sources, that at this point have not reached the commercial market, although they most certainly will given the results demonstrated to date.

The most widespread commercial application of glow discharge devices is in the area of atomic emission spectroscopy. In Chapter 2, Professor José Broekaert (University of Hamburg) describes the fundamental aspects of emission spectroscopy in general and how GD plasmas generate useful emission spectra. Comparison of operation mechanisms and analytical characteristics are made with other solids analysis methods. Also described in the chapter is the evolution of the common Grimm-type cell geometry and its many applications in bulk solids analysis. Methods of modifying the basic design in order to optimize the source characteristics are also discussed.

Chapter 3 presents the design considerations and methodologies employed in performing mass spectrometry of glow discharge devices. Professor Willard W. Harrison (University of Florida) and co-workers review the pertinent plasma processes responsible for the ionization of sputtered atoms and the roles of plasma parameters and operating modes in producing quantitatively useful mass spectra. The particular strengths and weaknesses of the different mass analyzer types are also presented. Finally, the methods of quantification for solids elemental analysis by GDMS are described.

While the majority of GD systems sold in the 1970s and 1980s were dedicated to the analysis of metallic specimens, the types of solid samples that could benefit from GD analysis extend across many different physical and chemical forms. In Chapter 4, Professor R. Kenneth Marcus (Clemson University) describes the underlying plasma physics which accompany the use of rf powering of GD sources and permit the analysis of electrically insulating materials. The results of comparative studies performed in a number of laboratories between rf and conventional dc powering modes are presented. Practical examples of the sorts of applications that rf powering permits include glass analysis, depth profiling of oxide coatings, and direct mass spectrometric analysis of polymeric materials.

The most compelling advantage of glow discharge sources over other solids analysis methods is the inherent ability to perform depth-resolved analyses in a rapid, yet well controlled manner. Dr Arne Bengtson (Swedish Institute for Metals Research) presents in Chapter 5 the fundamental and practical aspects of performing depth profile analysis using GD sources, particularly when employing optical emission detection. Plasma operation and control functions and also data acquisition parameters are discussed in detail. The concept of the emission yield

as a fundamental quantity for performing quantitative depth profiles is presented in detail along with a discussion of the common artifacts encountered and how they are remedied.

In Chapter 6, Dr Annemie Bogaerts and Professor Renaat Gijbels (University of Antwerp, Belgium) deal with their work on the modeling of analytical glow discharges. This includes the development of a fluid model and Monte Carlo simulation and also a particle-in-cell model. For analytical glow discharges, a hybrid model is shown to be very powerful and is used surprisingly well to predict current–voltage characteristics. Potential and electrical field distributions, densities and level populations of the plasma species, energies of the plasma species, sputtering profiles and even optical spectra can be calculated, which are in good agreement with experimental data. As the influence of various operational and cell parameters can be predicted, optimization of the construction of sources may greatly benefit from this work. It is also shown, however, that the acquisition of the required plasma characteristic data is very challenging and that progress here is necessary to make the agreement between the results of modeling and experimental data better still.

Probably the largest market sector employing GD spectrometries on a routine basis is the steel industry. Early acceptance took place by virtue of the relative freedom from the matrix of GD-OES in comparison with spark emission spectroscopy. In Chapter 7, Dr Kazutoshi Kakita (Nippon Steel Technoresearch Corporation) describes the current use of GD-OES in the steel industry. Aspects of method development including traceability and eventual verification are described in detail. Specific application examples include the depth-resolved analysis of galvanized steel, aluminized steel, and galvannealed steel. Practical considerations in obtaining valid profiles are presented along with examples of how GD-OES profiles can be used to explain metallurgical phenomena.

As mentioned previously, the introduction of the rf powering mode opens up many new areas of application for glow discharge analyses, particularly GD-OES. Dr Richard Payling (University of Newcastle, Australia) and co-workers from a number of industrial laboratories present the use of rf-GD-OES in the analysis of surfaces, coatings, and thin films in Chapter 8. The versatility of the method is demonstrated for a large array of applications that cut across many industrial sectors ranging from studies of alloy corrosion and hardening, to electronic multilayer materials and a variety of coating technologies. Many of the examples include the use of complementary physical and chemical analysis methods to solve the posed problems.

Of course, any discussion of the capabilities of a single analytical method cannot take place with the exclusion of the figures of merit for other techniques providing the same or complementary forms of information. Professor Kazuaki Wagatsuma (Tohoku University) presents in Chapter 9 a comparison of the attributes of glow discharge spectroscopies with a number of what might be termed ‘more traditional’ methods of surface and thin film analysis. Starting

with a baseline set of qualities for (principally) GD-OES, the most relevant of the other methods are discussed. Detailed descriptions of the underlying physics and analytical characteristics are presented for ion probe, electron probe, X-ray probe, and laser probe techniques. Finally, direct comparisons between GDS and secondary ion mass spectrometry (SIMS) and with Auger electron/photoelectron spectroscopies are made for the same samples. Actual analytical data are presented in the comparisons to highlight the respective performance characteristics of each method.

The analysis of samples of nuclear concern with glow discharge atomic spectrometry is treated in Chapter 10 by Dr Maria Betti (European Commission, JRC, Karlsruhe, Germany). For the applications of GD techniques for the determination of major and trace elements, as well as the matrix isotopic composition, dc-GDMS and rf-GD-OES instrumentation installed inside glove-boxes has been described for the handling of radioactive samples. The analysis of conductive samples has been described in addition to different approaches for the analysis of nonconductive samples. The latter includes the use of radio frequency powered sources, the use of a secondary cathode, and mixing with a binder conductive host matrix prior to briquetting. In the case of oxide-based samples, the employment of a tantalum secondary cathode acting as an oxygen getter is shown to reduce polyatomic ion formation and plasma quenching. Analysis of uranium oxide with respect to impurities and isotopic composition is reported and GDMS is shown to be competitive with TIMS.

The analysis of nonconducting materials in general is treated in Chapter 11 by Dr Annemie Bogaerts, Dr Wim Schelles and Professor René Van Grieken (University of Antwerp, Belgium). Here the features and use of the three methodologies mentioned above are discussed for a wide range of applications, referring to the respective literature. In the technique using metal powders as binder, special attention is given to the sample-to-host ratio. The influence of the particle size in the case of the analysis of powders is discussed, in addition to the presence of trapped gases in the pellets. Applications cited range from ores to glasses, vegetation to ceramic samples and meteoric residues. For the case of a conducting secondary cathode, the mechanism is discussed in detail. Attention is also paid to the material and geometry of the secondary cathode, and the discharge conditions and applications of the technique confined to GDMS work are discussed.

Driven by the highly international nature of commerce, there is an increasing need for standardization within given industrial and economic sectors. In the area of analytical chemistry, standardization can be thought of in terms of either methodology or reference materials. Dr Michael Winchester (National Institute of Standards and Technology, USA) describes both of these aspects of achieving accurate analytical results in Chapter 12. Standard methods adopted by a number of standards development organizations such as ASTM and ISO are presented for both GDMS and GD-OES. In addition, the various classifications and uses for reference materials and how they are developed are also described.

Traditionally, the development of glow discharge sources as tools for performing direct solids elemental analysis took place in parallel with developments of techniques for the analysis of solution samples including flames and atmospheric pressure plasma sources. While the kinetic temperature of a GD plasma is too low to achieve solution sample desolvation in the case of direct solution nebulization, there are a number of advantages that can be projected in using the sources for the analysis of samples originating in the solution phase. Professor R. Kenneth Marcus (Clemson University) describes in Chapter 13 the three general approaches to introducing solution samples into GD sources for subsequent analysis. Included in the discussion are two different means of introducing solutions as part of flowing streams such as encountered in liquid chromatography. The versatility of the GD source as a detector for elemental speciation is demonstrated in the analysis of a number of amino acid species.

Just as GD devices can be used to advantage as detectors for liquid chromatography, their use as detectors for gas chromatography (GC) also holds great promise. The coupling between the GC and a glow discharge is quite natural as no solvent load is imposed on the plasma and because the mobile phase is usually an inert gas that can sustain the plasma. In Chapter 14, Professor Joseph A. Caruso (University of Cincinnati) and Dr Lisa Milstein (RTI International) describe the coupling of gas chromatography with GDMS sources to effect a powerful new approach to elemental speciation of volatile organometallic molecules. The ability of the sources to achieve sub-picogram sensitivities while providing unambiguous mass spectra of species of environmental importance is demonstrated. Very important in these applications is the ability to 'tune' the fragmentation patterns of mass spectra to achieve different levels of information. Studies to date suggest that this approach holds much promise for speciation studies in environmental and biological chemistry.

In Chapter 15, Dr Rosario Pereiro, Dr Nestor G. Orellana-Velado and Professor Alfredo Sanz-Medel (University of Oviedo, Spain) treat the use of glow discharge atomic emission spectrometry as an alternative gas chromatographic detector. The favorable physical features of atomic emission spectrometry with a low-pressure discharge, such as low continuum background and high electron temperatures, indeed make it a promising spectrochemical source for the analysis of gases and volatilized analytes. Potentially, the glow discharge could offer similar and even better detection limits than other more common sources used as detectors for the direct analysis of gaseous samples or as a detector in gas chromatography. An important advantage of glow discharges when used for chromatographic detection are their low running costs. In the chapter, three approaches to the introduction of analytes into the discharge chamber in the gas phase are treated. First, the gaseous samples or liquid organic samples can be introduced after vaporization by thermal means. Second, a chemical reaction can be used to convert the analyte from a liquid sample to a volatile derivative. Finally, the glow discharge can be used as gas chromatographic detector

directly. Details about the source construction, types of cathodes and interfaces, the plasma operating conditions, and analytical performance both for dc and rf sources are discussed along with relevant examples.

Even though this book is devoted to the development and application of glow discharge sources for analytical spectroscopy, there are other means of producing low-pressure plasma sources that have favorable characteristics for speciation studies. In each of the approaches, the target plasma has very similar gas-phase characteristics to GD sources, as such very powerful ion sources for speciation studies are the result. Professor Hywel Evans (University of Plymouth) describes in Chapter 16 how a variety of powering schemes can result in analytically useful low-pressure (LP) plasma ion sources. Specifically, inductively coupled and microwave-induced plasmas can be configured to operated in the 1–10 Torr range. Rf microplasmas and flowing afterglows are also described. In comparison with their widely used atmospheric pressure cousins, MS sampling of these plasmas is easier from the instrumentation point of view. In addition, optical emission sampling is an effective means of GC detection.

In Chapter 17, Dr John Guzowski, Jr and Professor Gary Hieftje (Indiana University) treat the development of multidimensional ionization sources for plasma-source mass spectrometry and give an outlook on a very important direction of development for glow discharges. For chemical speciation, it is a common approach to couple a separation method with a selective and sensitive detection method such as mass spectrometry. Conventional atomic or molecular mass spectrometric ionization sources are ordinarily incapable of providing, by themselves, both elemental and molecular information. This limitation drastically increases the cost, time, and complexity associated with fully characterizing a sample. However, new ionization sources, among which are glow discharges, are being developed that can generate both atomic and molecular fragment ions, and have been coupled with a variety of mass spectrometers and separation techniques. The approaches being used in the development of these multidimensional ion sources are highlighted in this chapter. Ultimately, the goal is to develop a single ionization source that can provide both types of information during a single measurement, making it especially valuable as a chemical speciation and characterization tool.

In the development of this volume, it was the Editors' intention to put together a comprehensive overview of the quickly expanding area of glow discharge spectroscopies. It is hoped that the volume will be a useful reference source for those entering the field and practitioners alike.

1.5 REFERENCES

1. Paschen, F. *Ann. Phys.* 1916, **50**, 191.
2. Schuler, H. Z. *Phys.* 1929, **59**, 149.
3. Grimm, W. *Spectrochim. Acta, Part B* 1968, **23**, 443–454.

4. Belle, C. J.; Johnson, J. D. *Appl. Spectrosc.* 1973, **27**, 118–124.
5. Bengtson, A. *Spectrochim. Acta, Part B* 1985, **40**, 631–639.
6. Marcus, R. K.; Harville, T. R.; Mei, Y.; Shick, C. R., Jr. *Anal. Chem.* 1994, **66**, 902A–911A.
7. Fang, D.; Marcus, R. K. In *Glow Discharge Spectroscopies*, Marcus, R. K., Ed., Plenum, New York, 1993, Chapter 2.
8. Howason, A. M. *An Introduction to Gas Discharges*, Pergamon Press, Elmsford, NY, 1976.
9. Davis, W. C.; Marcus, R. K. *J. Anal. At. Spectrom.* 2001, **16**, 931–937.
10. Boumans, P. W. J. M. *Theory of Spectrochemical Excitation*, Hilger & Watts, London, 1966.
11. Broekaert, J. A. C. *Analytical Atomic Spectrometry with Flames and Plasmas*, Wiley-VCH, Weinheim, 2001.